

ON THE NATURE OF EXTRA REFLECTIONS IN THE LAUE PHOTOGRAPHS OF SOME DIAMONDS OF KNOWN RELATIVE FLUORESCENCE EFFICIENCIES

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Plates 1A, 1B, 1C, & 1D.

ABSTRACT. The positions and approximate relative intensities of extra spots accompanying the $\{111\}$ reflection in the Laue photographs of eleven specimens of diamond have been determined using a Seifert X-ray tube provided with a copper target and nickel filter and running at 30 Kv, 28 mA. In order to measure the directions of extra reflections accurately in some cases the front surface of the crystals as dusted with powdered NaCl, so that the Debye-Scherrer pattern of NaCl was superimposed on the Laue photographs. The specimens studied were used by Bishui (1950, 52) in previous investigations on the relative intensities of the fluorescence band at 4156 \AA and on the ultraviolet absorption limits. The results show that all the specimens excepting D 6 possess partial mosaic structure, so that they produce extra reflections from $\{111\}$ planes of different intensities in the direction making an angle $2\theta_B$ with the incident rays when the disorientation from the Bragg angle θ_B is less than 3° .

It is observed that neither the intensities of the extra reflections nor those of the extra reflections in other directions present in the Laue photographs of some of the crystals can be correlated either with the intensity of the band at 4156 \AA or with the impurity present in the crystals. Also, these intensities cannot be correlated with the respective thicknesses of the specimens.

INTRODUCTION

It was first shown by Lonsdale and Smith (1941) that the secondary X-ray reflections consisting of groups of extra spots observed in the Laue photographs of diamonds of Type I do not appear in the Laue photographs of diamonds of Type II. Later, Lonsdale (1941) reviewed the existing theories put forward to explain the origin of these secondary extra reflections and pointed out that all the observed facts could not be explained satisfactorily by any of the existing theories. Guinier (1942) put forward a new theory in which he suggested that partial irregularities of spacing along the cube edges might give rise to these extra reflections. Lonsdale (1948) studied the divergent-beam X-ray photographs of specimens of diamond of Type I and Type II and observed that diamonds of Type I produced bad divergent-beam photographs which showed that the crystals had perfect structure. On the other hand, all Type II diamonds studied by her gave excellent divergent-beam photographs. So, she pointed out that

although Guinier's hypothesis could explain many features of the extra spots satisfactorily it was difficult to understand why such partial irregularity in spacing should occur only in diamonds having a perfect structure and should be absent in Type II diamonds having a mosaic structure. More recently, Grenville-Wells (1952) studied the divergent-beam photographs of 38 specimens of diamond of different qualities and also the relative intensities of the fluorescence and the secondary extra reflections produced by these diamonds in order to find out whether the texture of the specimens could be correlated with their counting properties, which had been determined along with the ultraviolet transparency earlier by Champion (1952), and also with the intensity of extra reflections produced by these diamonds. The results obtained by her do not confirm the conclusions drawn by Lonsdale (1942) that only diamonds having perfect structure produce intense extra reflections and those having mosaic structure do not produce such reflections. Some of the specimens produced neither good divergent-beam photographs nor secondary extra reflections while some other specimens producing good extra reflections yielded good divergent beam photographs. She also proved conclusively that the intensity of fluorescence of the diamonds could not be correlated either with texture or with the intensity of extra reflections.

There are, however, several points which are not quite clear from the results reported by Grenville-Wells (1952). First, while studying the extra reflections, she considered only the intensities without measuring accurately the directions in which these extra reflections took place. It is not known whether some of the specimens giving good divergent beam photographs also produced sharp extra reflections in the direction making an angle equal to double the Bragg angle with the incident X-rays, indicating thereby the existence of mosaicity in the crystals. Secondly, as regards the fluorescence she probably estimated the total intensity of the light emitted by the crystals without considering its spectral distribution. It was shown by Bishui (1952) that diamonds should not be classified as Type I and Type II on the criterion of mere transparency in the ultraviolet region, because specimens having absorption limit at 2300 \AA , but showing absorption bands at 2360 \AA and 2363.5 \AA give strong fluorescence band at 4156 \AA and these should be classified as Type I diamond. Bishui (1950, 52) estimated the relative fluorescence efficiencies at 4156 \AA of 14 specimens of diamond and also studied the ultraviolet absorption limits of the specimens. The present investigation was undertaken to find out whether there was any correlation between the intensity of the band at 4156 \AA and intensities of the extra reflections given by these diamonds. It was also intended to attempt at a separation of the reflection due to mosaicity from other types of secondary reflections not satisfying Bragg's law for $\text{Cu K}\alpha$ radiation and to find out whether these residual extra reflections can be correlated with either the intensity of the band at 4156 \AA or with the ultraviolet transparency.

EXPERIMENTAL

The Laue photographs were taken with a cylindrical camera having a radius of about 5.1 cm in order to measure the angles accurately. The divergence of the X-ray beam incident on the crystal was about $2^{\circ}18'$. A Seifert X-ray tube giving 28 m.A. at 30 Kv and provided with copper anticathode was used in this investigation. A nickel filter was used to cut off the $\text{Cu } K\beta$ radiation. An exposure of 2 hours was required for getting intense Laue photograph of diamond. As the crystals were all of large size the Laue spots were elongated in the direction at right angles to the plane of incidence corresponding to the width of the incident beam. The horizontal width of the vertical Laue spots is, however, determined mainly by the thickness of the crystals, because two divergent rays, reflected by two parallel planes in the crystal produce two convergent rays, the angle of convergence being equal to the angle of divergence of the incident rays. The distance of the point of convergence is $D \cos 2\theta$, where D is the distance of the slit from the crystal and θ is the glancing angle. The diamonds used in the present investigation are the same as those used by Bishui (1950,52). The thickness of crystals varies from .647 mm to 2 mm as shown in Table I. The ultraviolet absorption limits of most of these diamonds are also given in this table.

The specimen D 13 gave no fluorescence at 4156 \AA and D 4 produced an extremely weak band at this position. So, these two were classified as Type II diamonds. D 11 and D 14 exhibited absorption bands at 2360 \AA and 2363 \AA and gave strong fluorescence bands. These two diamonds were classified by Bishui as diamonds of Type I.

TABLE I

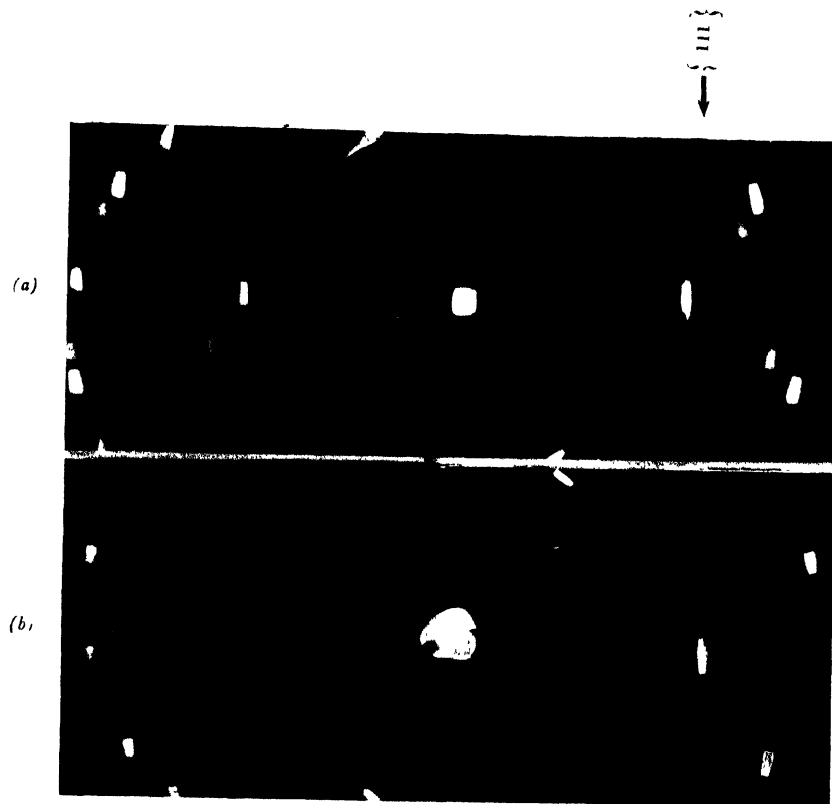
Specimen used	thickness in mm.	UV absorption limit in A.U.	
D 1	1.5	--	
D 4	1.5	2300	
D 6	2.0	--	
D 7	1.353	2560	
D 8	1.30	3000	
D 9	0.8	2550	
D 10	1.092	2810	
D 11	0.952	2270	(absorption bands at 2360 etc.)
D 12	0.647	2720	
D 13	0.838	2240	
D 14	0.812	2300	(absorption bands at 2360 etc.)

Preliminary investigations showed that some of the specimens produced extra reflections in the directions making an angle $2\theta_B$ with incident rays, where θ_B is Bragg angle for {111} planes of diamond for Cu $K\alpha$ radiation. In order to verify this, attempts were made to measure the angles correctly by superimposing Debye-Scherrer photographs of rocksalt on the Laue photographs. This was done by dusting the front surface of the specimen with fine powders of chemically pure NaCl. It was found that when both the surfaces were dusted in this way two sharp ring systems of NaCl were produced corresponding to the two surfaces separated by the thickness of the crystal. This happens because in the case of reflection by powdered crystal, the partial focussing effect observed in the case of Laue spots is absent. So, care was taken to put a narrow line of powdered NaCl on the surface of the crystal through which the X-rays emerged. In measuring the distance of the crystal from the film, half the thickness of the crystal was added to the distance obtained from the position of the Bragg reflection from the {220} plane of NaCl. As this spacing of NaCl and that of {111} planes of diamond are near to each other the angle between the reflections from these two planes could be measured very accurately by this method. For each diamond several Laue photographs were taken with different disorientations from the Bragg angle. The angle between the direction of the incident beam and that of the Laue spot due to {111} plane and the corresponding angle for the extra reflection accompanying it were measured accurately in each case. Altogether eleven specimens were studied.

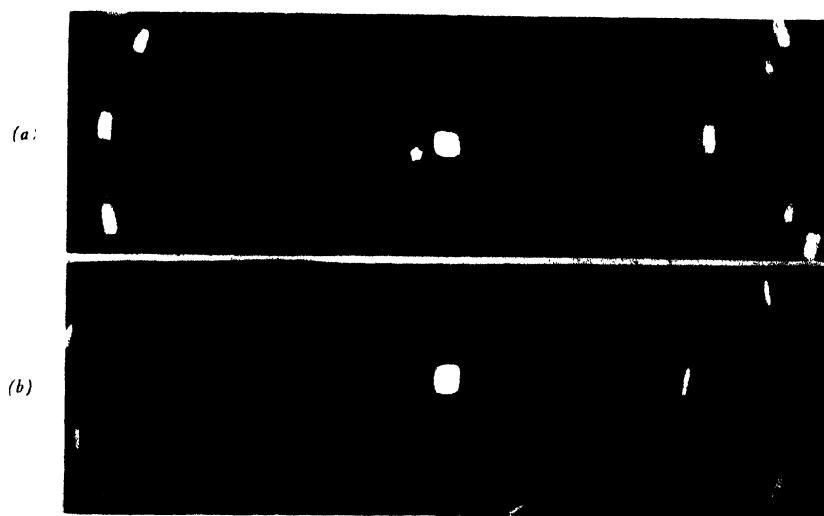
RESULTS AND DISCUSSION

Some of the Laue photographs are reproduced in Plate I to show that in some of the photographs the extra reflections are extremely sharp and their positions could be determined very accurately. The results are tabulated in Table II in which 2θ is the angle made with the incident rays by the ray corresponding to the Laue spot and $\theta + \phi$ is the angle made similarly by the extra reflection. The approximate intensities of extra reflections are indicated as strong, medium weak and very weak by the letters s, m, w and v.w respectively. The widths of the extra reflections are given as sharp, broad and diffuse. The intensities of the fluorescence band at 4156 Å are taken from the results reported by Bishui (1950, 52). As regards D1 and D4, absolute fluorescence efficiencies were not determined by Bishui, but visual examination of the spectrograms shows that the value of the constant K is about 6.

It can be seen from Table II that all the specimens, excepting D6, give extra reflections in the direction making an angle of about $43^\circ 56'$ with the incident rays for different positions of the Laue spot. This shows that these extra reflections are produced by the Bragg reflection of Cu $K\alpha$ rays from the {111} planes even when the glancing angle is slightly different from $21^\circ 58'$. This is possible

Fig. 1. Diamond D 1. $\{110\}$ vertical.

(a) $2\theta = 39^{\circ}20'$ $\theta + \varphi = 42^{\circ}51'$
 (b) $2\theta = 42^{\circ}29'$ $\theta + \varphi = 43^{\circ}57'$

Fig. 2. Diamonds D 4 and D 9. $\{110\}$ vertical.

(a) D 4 ; $2\theta = 45^{\circ}51'$ $\theta + \varphi = 43^{\circ}51'$
 (b) D 9 ; $2\theta = 41^{\circ}36'$ $\theta + \varphi = 43^{\circ}58'$

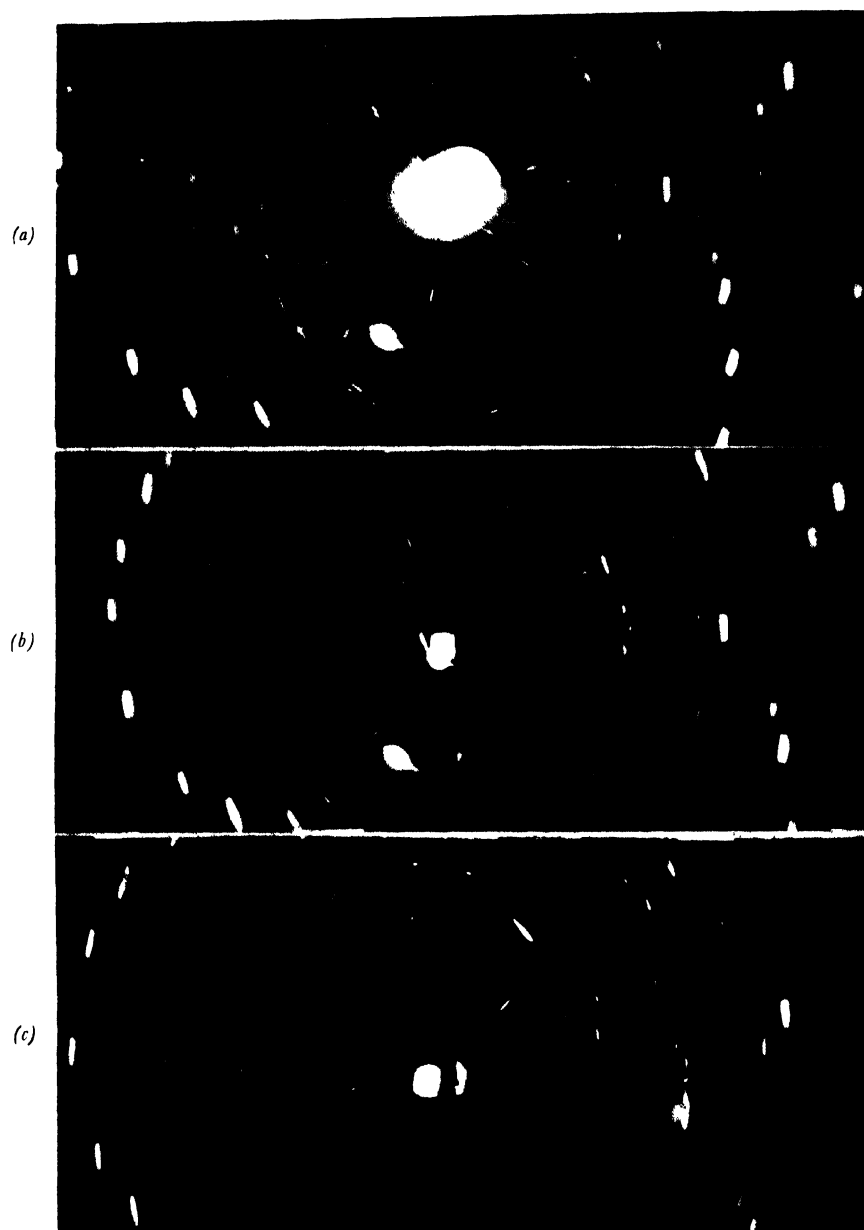


Fig. 3. Diamonds D 7 and D 11. $[110]$ vertical.

- (a) D 7 ; $2\theta = 40^{\circ}35'$, $\theta + \varphi = 43^{\circ}45'$
(b) D 7 ; $2\theta = 49^{\circ}40'$, $\theta + \varphi = 43^{\circ}50'$
(c) D 11 ; $2\theta = 45^{\circ}48'$, $\theta + \varphi = 43^{\circ}58'$

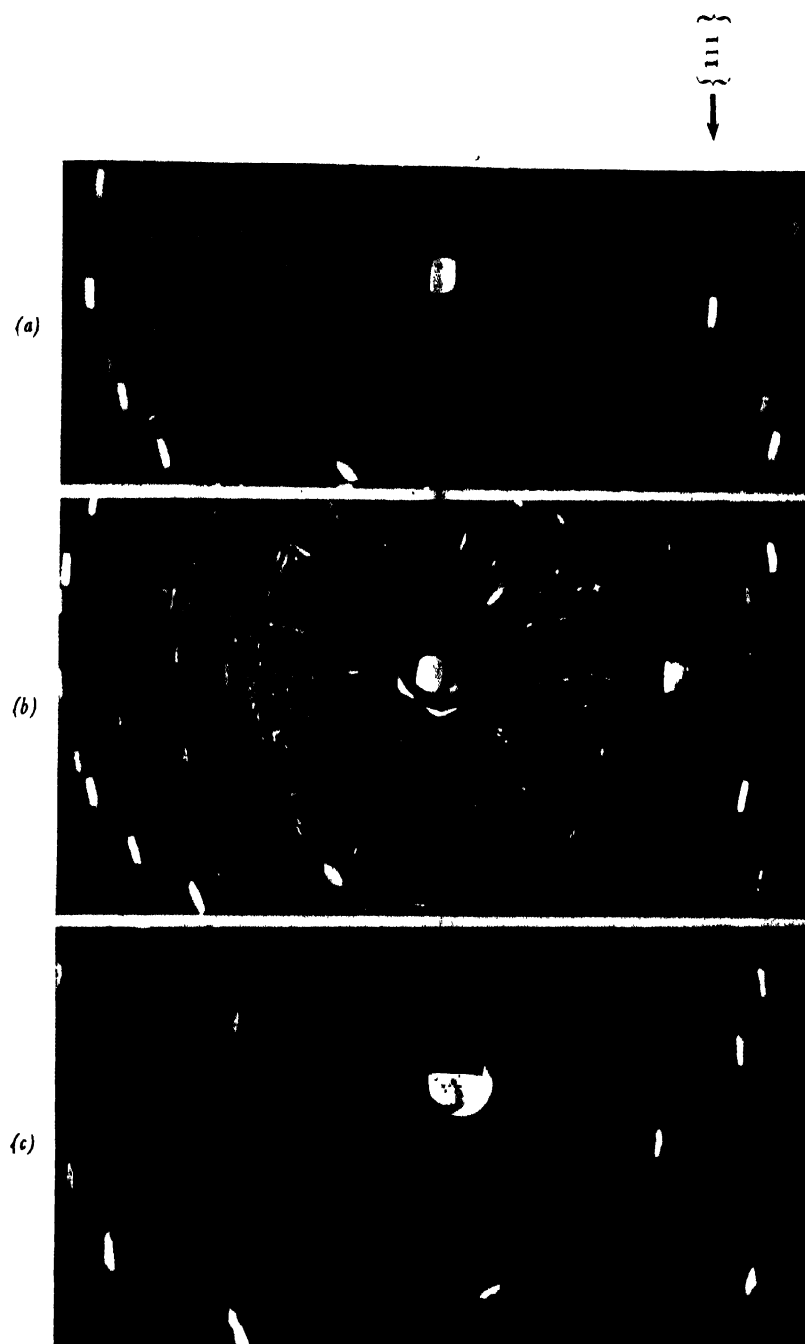


Fig. 4. Diamonds D 8 and D 10. $[\bar{1}10]$ vertical.

- | | |
|--|------------------------------------|
| (a) D 8 ; $2\theta = 47^{\circ}30'$, | $\theta + \varphi = 43^{\circ}52'$ |
| (b) D 8 ; $2\theta = 41^{\circ}33'$, | $\theta + \varphi = 43^{\circ}48'$ |
| (c) D 10 ; $2\theta = 39^{\circ}26'$, | $\theta + \varphi = 43^{\circ}56'$ |

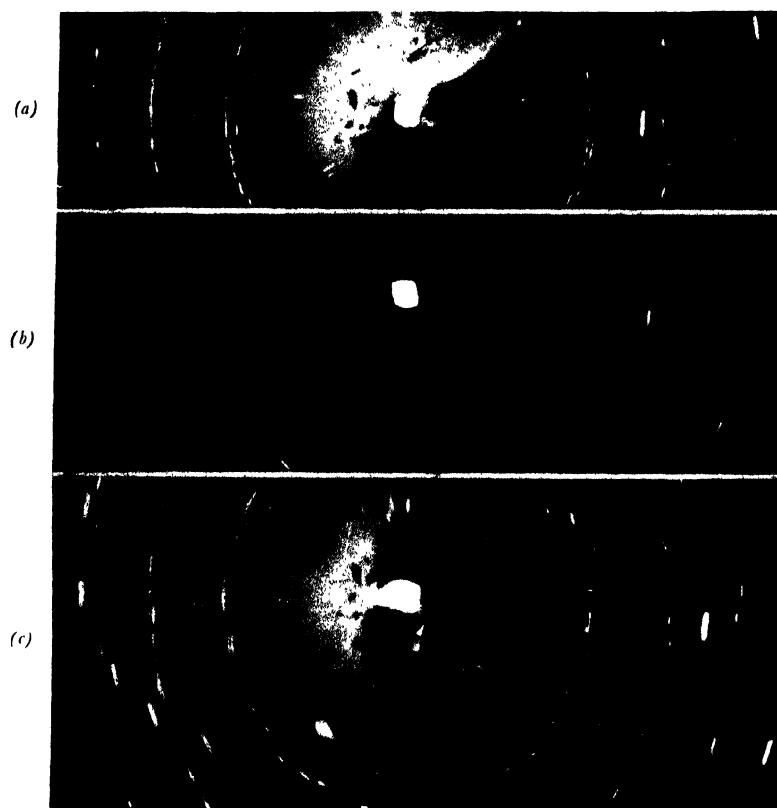


Fig. 5. Diamond D 12. $[110]$ vertical.

- (a) $2\theta = 40^\circ 48'$, $\theta + \varphi = 43^\circ 58'$
 (b) $2\theta = 41^\circ 36'$, $\theta + \varphi = 43^\circ 56'$
 (c) $2\theta = 51^\circ 42'$, $\theta + \varphi = 46^\circ 1'$

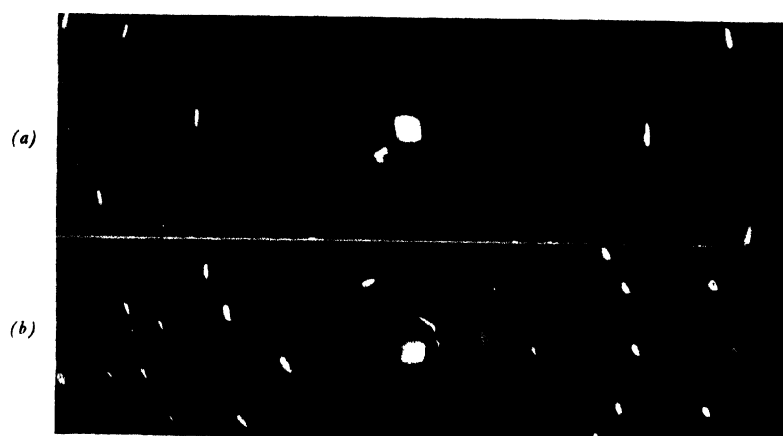


Fig. 6. Diamonds D 13 and D 14. $[110]$ vertical.

- (a) D 13 ; $2\theta = 41^\circ 36'$, $\theta + \varphi = 43^\circ 57'$
 (b) D 14 ; $2\theta = 41^\circ 2'$, $\theta + \varphi = 43^\circ 57'$ (smaller camera)

TABLE II

Specimen No.	2θ	$\theta + \varphi$	Width	Intensity	I_{4156}/I_R	Remarks
D 1	37°39'	42°29'	B and D	w	57/ $K \sim 9.5$	K is an unknown constant. Visual comparison of the spectrograms shows that $K \approx 6$.
	39°20'	42°51'	B and D	m	"	
	42°29'	43°57'	sharp	s	"	
D 4	45°51'	43°51'	B and D	w	1	
	39°48'	42°56'	"	v.w.	"	
D 6	38°9'	42°45'	B	v.w.	54/ $K \approx 9$	
D 7	39°35'	43°42'	sharp	w	5.2	
	40°35'	43°45'	"	m	"	
	49°40'	43°50'	"	m	"	
D 8	36°37'	42°34'	sharp	w	1.5	
	41°33'	43°48'	sharp	s	"	
	45°44'	43°50'	"	s	"	
	47°30'	43°52'	"	s	"	
	51°10'	43°57'	B	m	"	
D 9	41°36'	43°58'	B	m	9.26	
	37°32' (sharp)	41°58'	B	v.w.	"	
D 10	39°26'	43°56'	B	w	8.4	
	41°58'	43°59'	sharp	m	"	
	47°54'	44°58'	sharp	m	"	
	35°49'	43°38'	V.B.	v.w.	"	
D 11	42°9'	43°58'	B	s	7.1	
	41°22'	43°58'	B	w	"	
	47°12'	43°58'	B	v.w.	"	
	45°48'	43°58'	sharp	strong	"	
D 12	40°48'	43°38'	B	s	3.8	
	45°51'	44°0'	B	v.s.	"	
	51°42'	46°1'	sharp	w	"	
	35°45'	43°3'	B	w	"	
	41°36'	43°28'	sharp	s	"	
		43°56'	"	m	"	
	41°8'	43°3'	sharp	s	"	
D 13		43°58'	"	m	"	
	41°36'	43°57'	B	w	0	
	42°43'	43°59'	sharp	m	"	
D 14	41°0'	43°17'	B	w	"	
	36°51'	43°26'	B	v.w.	6	
	41°2'	43°57'	B	w	"	

only when there is mosaicity in the crystal and in a small volume of the crystal the {111} planes make a small angle with those planes in the major portion of the crystal. Some of the specimens, however, give extra reflections in other directions and these cannot be attributed to mosaicity of the crystals.

It can clearly be seen, however, from the data given in Table II that neither the mosaicity of the crystal indicated by the presence of extra reflection in the direction making the angle $43^{\circ}56'$ with the incident rays nor the intensity of the extra reflection in other directions can be correlated with the intensity of the fluorescence band at 4156 \AA . The intensity of this band is very small in the case of D 4, and D 13 does not exhibit this band at all, but the extra reflection due to mosaicity is present in both the cases. Also the intensity of the band due to D 8 or D 12 is much smaller than that of the band due to any of the crystals D 7, D 9 and D 10, but the extra reflections due to mosaicity given by D 8 and D 12 are much stronger than those given by the latter crystals. As regards the extra reflection in other directions it is absent in the case of D 11 and D 7, but the intensity of the fluorescence band is large. Also, the extra reflections due to D 6 and D 14 are very weak, but the fluorescence band is very strong. On the other hand, D 13 does not show any fluorescence at 4156 \AA , but it shows weak extra reflections in the direction $43^{\circ}17'$. It is thus evident that the fluorescence band and the extra reflections are produced by two entirely different causes.

It was pointed out by Bishui (1952) that the fluorescence band at 4156 \AA is produced by a particular type of impurity which produces two ultraviolet absorption bands at 2360 \AA and 2363.5 \AA respectively. The results obtained in the present investigation show that the amount of these impurities does not depend on either the partial mosaicity of the crystal or on the irregularities which produce extra reflections in directions other than that making an angle $2\theta_B$ with the incident rays. It was also pointed out by him that other impurities which are not responsible for the production of the fluorescence band at 4156 \AA are present in most of the specimens of diamond and produce a shift in the ultraviolet absorption limit towards longer wavelengths. As D 13 produces weak extra reflections due to partial mosaicity as well as those due to other irregularities and is a specimen of diamond containing absolutely no impurity, it is evident that the defects in the structure mentioned above does not depend much on the presence of impurity, but it appears from Tables I and II that any kind of impurity tends to enhance the formation of mosaic blocks in the crystal. It might be pointed out that the extra reflection in directions other than that making an angle $2\theta_B$ with incident rays observed in the present investigation cannot be attributed to thermal scattering, because these are very weak in the case of some of the crystal such as D 8 and D 11 and are present with large intensities in other cases e.g., D 1, D 10 and D 12. Also, these intensities cannot be correlated with the thickness of the crystals. These extra reflections may be due to permanent irregularities in the

spacing along cube edges, as pointed out by Guinier (1952). It is quite clear from the data given in Table II for D 12 that both partial mosaic structure and the irregularities in spacing can be present simultaneously in a single specimen. This particular specimen is a thin triangular plate of thickness 0.647 mm and it is observed that with gradual increase in the disorientation from the Bragg angle the two sharp reflections corresponding to the mosaic structure and the other type of irregularity are gradually separated from each other, and when 2θ is diminished to $35^{\circ}45'$ the intensities of both these reflections diminish abruptly. So, the fraction of the volume in which the $\{111\}$ planes make an angle of about $4^{\circ}5'$ with these planes in the rest of the volume is very small. It is found that in most of the specimens, this angle lies within 3° . The partial mosaic structure indicated above is different from the mosaic structure indicated by divergent-beam photography. In the latter case the orientation of the planes varies gradually and continuously within narrow limits throughout the whole volume of the crystal, so that all the rays in the incident X-ray beam making a small angle upto about 1° or 2° with each other are reflected by the planes satisfying Bragg condition. In the present case the crystals showing weak reflections due to mosaic structure possess such mosaic blocks only in small parts of the whole volume.

Finally, it may be pointed out that these conclusions are generally in agreement with those drawn by Grenville Wells (1952) who studied only the integrated intensities of the total fluorescent light and the intensities of the extra reflections without giving their actual directions. Probably some of the extra reflections observed by her in the case of the diamonds giving good divergent-beam X-ray photographs were actually in the direction making an angle $2\theta_B$ with the incident rays. As regards the intensities of fluorescence given by her in Column (3), these are indicated as zero in the case of many of the diamonds showing ultraviolet absorption limit longer than 2400 \AA . It is doubtful whether the intensities of the fluorescence band 4156 \AA is zero in all these cases, because previous workers have observed the fluorescence band in the case of all crystals having such absorption limits in the ultraviolet region.

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